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(54) Title: **POLYMERIC SURFACTANTS**

(57) Abstract: Amide surfactant compound of the formula (I): $R^1-CO-NR^2R^3$, where R^1 is a polymeric hydrophobe group; R^2 is a group $CH_2-(CHOR^4)_n-CH_2OR^4$ where n is from 3 to 6 and R^4 is hydrogen, C_1 to C_6 alkyl or a saccharide residue, containing at least 2 free hydroxyl groups; and R^3 is hydrogen, C_1 to C_{22} hydrocarbyl, substituted alkyl, or R^3 is independently as defined above for R^2 , are useful as emulsifiers and/or stabilisers for water in oil emulsions, or as dispersants for solids in aqueous or non-aqueous liquids. Particular end use applications include as emulsifiers, stabilisers or dispersants in making polyacrylamide, particularly for water treatment, by inverse emulsion polymerisation; emulsion explosives; personal care compositions including an aqueous phase dispersed or emulsified in an oil phase; agrochemical emulsions and concentrates, and cutting fluid emulsions and concentrates.

Polymeric Surfactants

This invention relates to polymeric surfactants and in particular to such surfactants where the hydrophile is polyhydroxy hydrocarbyl, particularly sugar derived and the hydrophobe is polymeric hydrocarbyl or polyester. The invention includes applications of such surfactants including as emulsifiers in polymerisation reactions, in emulsion explosives, in cosmetic emulsions, in agrochemical emulsions and suspoemulsions, in oilfield applications and in metal working, for the dispersion of solids, and as oil field drilling fluid additives.

Polymeric surfactants are known in which the hydrophobe is polymeric hydrocarbyl e.g. a polyisobutylene group, as described in EP 0004426 A and EP 0214758 A or polyester e.g. a polyhydroxy fatty acid residue, as described in GB 1469531 and EP 0000424 A. These surfactants have been used successfully in widely differing end use applications particularly under demanding conditions. Although they have been technically successful, wider applicability has been restricted by the nature of the components or the relatively severe reaction conditions under which they are made. For example, the materials described in EP 0000424 A include a hydrophile which is derived from ethylene oxide and there are demands for surfactants that do not use ethylene oxide derivatives.

This invention is based on our discovery of surfactants using polymeric hydrophobes and polyhydroxy hydrocarbyl hydrophiles which can be made without ethylene oxide and which do not require extreme conditions for their synthesis.

Accordingly, the present invention provides an amide surfactant compound of the formula (I):



where:

- R^1 is a polymeric hydrophobe group, in which the units that make up the polymer contain at least 4 carbon atoms, there are at least 5 units in the polymeric group and the polymeric group contains at least 30 carbon atoms in total;
- R^2 is a group $CH_2-(CHOR^4)_n-CH_2OR^4$ where n is from 3 to 6 and R^4 is hydrogen, C_1 to C_6 alkyl or a saccharide residue, containing at least 2, usually at least 3 and desirably at least 4, free hydroxyl groups;
- R^3 is hydrogen, C_1 to C_{22} hydrocarbyl, a substituted alkyl group e.g. a hydroxy or alkoxy substituted alkyl group, or R^3 is independently as defined above for R^2 .

The compounds of the formula (I) are surfactants. As they have a relatively large hydrophobe they are relatively hydrophobic materials and typically have relatively low HLB values e.g. in the range 5 to 8 and particularly 6 to 7. As such they are useful in making and/or stabilising water in oil emulsions and/or dispersing particulates in liquid media, particularly organic media for a variety of

end use applications.

The hydrophobe in compounds of the formula (I) can be a hydrocarbyl polymeric group containing at least 30, and usually at least 50, carbon atoms. Such groups may contain up to 1000, but more usually up to 500 carbon atoms. The hydrocarbyl polymeric group is typically based on an olefin polymer. Particularly suitable monomers are butylenic monomers especially *iso*-butylene. The hydrocarbyl group may be linked directly to the carbonyl group in formula (I) or indirectly through a linking group. An especially convenient way of linking the hydrocarbyl to the carbonyl group is to link the hydrocarbyl group to a succinic acid group. The succinic acid group provides two carboxyl functions and there are two other carbon atoms to which the hydrocarbyl group can be linked.

Such compounds can be made by an ene reaction between the corresponding hydrocarbyl olefin and maleic anhydride to give a hydrocarbyl substituted succinic anhydride that can be further reacted to make the surfactant. In such compounds, at least one of the carboxyl groups of the succinic acid group is linked to a hydrophile group. The other one may be a free carboxyl group or a salt or it can be linked directly or indirectly to a further group which may be a hydrophile, a hydrophobe or other group.

Accordingly, the invention particularly includes amide surfactant compounds of the formula (Ia):



where

R^{1a} is a polymeric hydrophobe including a polyisobutylene group particularly containing an average of from 40 to 200 carbon atoms; and R^2 and R^3 are as defined above.

In particular in formula (Ia), the group R^{1a} is of the formula:



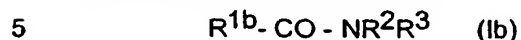
where

one of R^{5a} and R^{5b} is a hydrogen atom and the other is a polyisobutylene group particularly containing an average of from 40 to 200 carbon atoms; and R^6 is a group - OX where X is hydrogen atom, a metal, an amine or a hydrocarbyl group, particularly a C_1 to C_{20} hydrocarbyl group, especially an alkyl group; a hydroxyalkyl group, particularly a C_2 to C_6 hydroxyalkyl group, especially a hydroxyethyl, particularly 2-hydroxyethyl, or hydroxypropyl, particularly 3-hydroxypropyl, group; an alkoxyalkyl group, particularly a $(C_1$ to $C_4)$ alkoxy(C_2 to C_6)alkyl group, especially a 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, or 3-ethoxypropyl group; or R^6 is a hydrophilic group in particular an amido group and especially a group of the formula $-NR^2R^3$ where R^2R^3 are each independently as defined above.

Such groups will usually be derived from a polyisobutylene substituted succinic acid moiety - where

the group R^{1a} and the adjacent carbonyl group form such a succinyl residue.

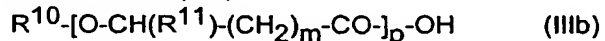
The hydrophobe may also be derived from a polyester residue, when it is typically a residue derived from a polymerised hydroxy fatty acid. Thus the invention further includes amide surfactant compounds of the formula (Ib):



where

R^{1b} with the adjacent carbonyl group is a residue of polyhydroxycarboxylic acid polyester group, containing an average of from 50 to 200 carbon atoms; and R^2 and R^3 are as defined above.

- 10 In particular the polyhydroxycarboxylic acid polyester from which the group R^{1b} is derived is an acid of the formula (IIIb):



where

- R^{10} is hydrogen or the residue of a C_2 to C_{22} fatty acid;
 15 R^{11} is hydrogen or a C_1 to C_{15} alkyl group;
 m is from 4 to 20; and
 p is on average from 4 to 20.

- Particularly, the polyhydroxycarboxylic acid can be derived from C_6 to C_{20} , hydroxycarboxylic acids (or their lactones) including 6-hydroxyhexanoic acid (or ϵ -caprolactone, more usually called
 20 caprolactone), 4-hydroxydecanoic acid (or γ -decanolactone), 5-hydroxydecanoic acid (or δ -decanolactone), 5-hydroxydodecanoic acid (or δ -dodecanolactone), 12-hydroxydodecanoic acid and 12-hydroxystearic acid, particularly caprolactone and/or 12-hydroxystearic acid. The polyester can be a homopolymer or a copolymer of different hydroxycarboxylic acids. In particular the polyhydroxycarboxylic acid is a poly-12-hydroxystearate, poly-6-hydroxyhexanoic acid (poly-
 25 ϵ -caprolactone, usually called polycaprolactone), a mixture of such polyesters, or a mixed polyester. Typical commercially available hydroxystearic acid contains stearic acid which during polymerisation acts as a chain terminating agent. The content of stearic acid can be used to control the polymer chain length for polymers made using hydroxystearic acid. The polyhydroxycarboxylic acid will typically on average contain from about 50 to about 200 carbon
 30 atoms. Mixed polyesters can block or random (statistical) copolymers made by copolymerising the respective hydroxycarboxylic acids particularly hydroxystearic acid (usually 12-hydroxy stearic acid) and caprolactone (or 6-hydroxyhexanoic acid). Mixed polyesters of this type are described in US 5700395. When mixed chain polyesters are used each hydroxyfatty acid will usually contribute at least 10 mole% of the residues in the chain so that in a binary copolymer polyester the relative
 35 molar proportions of the hydroxyfatty acid residues will typically be from 90:10 to 10:90.

The group R^2 is a group $CH_2-(CHOR^4)_n-CH_2OR^4$ where n is from 3 to 6 and R^4 is hydrogen, C_1 to C_6 alkyl or a saccharide residue, such that the group includes at least 2, usually at least 3 and desirably at least 4, free hydroxyl groups. Particularly R^2 is an open chain tetratol, pentitol, hexitol or heptitol group. Especially desirably, R^2 is the residue of, or a residue derived from glucose, fructose or sorbitol, or a disaccharide such as maltose or palitose or a higher oligosaccharide. It is particularly convenient that R^2 is the residue of a reducing sugar, because the amines can be made by straightforward reductive alkylation reactions on ammonia or an amine H_2NR^3 .

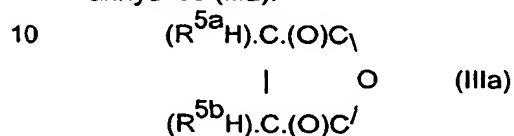
In the compounds of the formula (I) of and used in this invention the group R^2 is present as or as part of the hydrophile. Thus it will usually be desirable that the hydrophilicity of this group is not unduly reduced. Where R^2 is the residue of, or a residue derived from, an oligosaccharide it can be considered as an open chain mono-saccharide derived group or residue with a saccharide or oligosaccharide substituent which may be cyclic or a chain of cyclic residues. Particularly useful R^2 groups are derived from glycoses and are of the formula: $-CH_2-(CHOH)_4-CH_2OH$, e.g. corresponding to residues from glucose, mannose or galactose. In this case the group $-NR^2R^3$ is of the formula: $-NR^3-CH_2-(CHOH)_4-CH_2OH$ and the group is conveniently called a glycamine group. Most commonly the group R^2 will be derived from glucose and the corresponding amines may be called glucamines (as they will usually be made from glucose) or sorbitylamines (as they are no longer unsaturated). Strictly, such compounds are derivatives of 1-deoxyglycitols (and 1-deoxyglucitols) and can be referred to as 1-deoxyglycetylaminines (and 1-deoxyglucitylaminines) or as corresponding aminoglycitols (and aminoglucitols).

The group R^3 can be a hydrocarbyl group (see further below) or it can be as defined for R^2 in which case the amine function provides two hydrophilic polyhydroxy hydrocarbyl groups. In this case, the two groups of the formula R^2 will often be (but need not be) the same, as it is usually easier to make the symmetrical polyhydroxy hydrocarbyl substituted amine intermediate. Where the group R^3 is a hydrocarbyl group, it is desirably an alkyl or alkenyl group, and typically it has from 1 to 30, more usually from 1 to 22, carbon atoms. R^3 can be a blocking group (mainly used to keep the synthesis straightforward), as when R^3 is a lower e.g. C_1 to C_6 , alkyl group, particularly a methyl or ethyl group. R^3 can be a longer chain e.g. C_6 to C_{30} , particularly a C_8 to C_{22} alkyl, group and such a longer chain group will tend to act as a secondary hydrophobe. R^3 can also be a substituted alkyl group e.g. a hydroxy or alkoxy substituted alkyl group, particularly a C_2 to C_6 alkyl group which is hydroxy substituted e.g. a hydroxyethyl, particularly 2-hydroxyethyl, or hydroxypropyl, particularly 3-hydroxypropyl, group, or a C_1 to C_6 alkyl group substituted with an alkoxy, particularly a C_1 to C_6 alkoxy and especially a methoxy, ethoxy or propoxy, group, so that the alkoxyalkyl group is particularly a 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, or 3-ethoxypropyl group. The additional hydroxyl group or oxygen atom may provide a modest

increase in water solubility. R^3 can also be an aralkyl group, particularly a C_7 to C_{12} aralkyl group, such as a benzyl group.

The compounds of the invention can be made by reacting an acid functional precursor including the polymeric hydrophobe with an amine of the formula (II): $H - NR^2R^3$, where R^2 and R^3 are as defined above, under amide synthesis conditions. The acid reacting precursor can be an acid of the formula (III): $R^1 - COOH$ where R^1 is as defined above, or a reactive derivative of such an acid.

Where the polymeric hydrophobe in the product surfactant is a group $R^6OOC-(CHR^{5a})-(CHR^{5b})-$, as defined above, the acid reacting precursor will usually be a corresponding substituted succinic anhydride (IIIa):

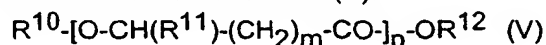


Such substituted succinic anhydrides where the polymeric group R^{5a} or R^{5b} is polyisobutylene are commonly described as Poly/soButyleneSuccinic Anhydrides (PIBSA's). Generally in this case the amidation reaction is straightforward and can be carried out at moderately elevated temperatures e.g. 80 to 150°C, particularly from 130 to 140°C, optionally with a solvent or diluent, such as mono-propylene or hexylene glycol or paraffin oil, and will not usually require the use of a catalyst although a catalyst, such as a transition metal alkoxide, may be used.

Where the desired final product is a bis-amide of an anhydride intermediate, such as PIBSA, the synthesis will generally be via a bis-ester intermediate by reacting an anhydride, such as PIBSA, with two moles of alcohol, particularly a short chain alcohol e.g. a C_1 to C_6 alcohol such as methanol or ethanol, to form a bis-ester, and subsequently reacting the bis-ester with a suitable amine under amidation conditions. Similarly amide ester products will typically be made by first reacting the anhydride with an alcohol corresponding to the ester group in the final product and then esterifying the remaining carboxyl group with an alcohol particularly a short chain alcohol e.g. a C_1 to C_6 alcohol such as methanol or ethanol, to form an asymmetric bis-ester and subsequently reacting the bis-ester with a suitable amine under amidation conditions displacing the second alcohol residue.

Where the hydrophobe is derived from a polyester residue and in particular for surfactants of the formula (Ib) above, although theoretically the free acid can be reacted directly with the amine of the formula (II), the reaction tends not to go to completion and side reactions occur leading to other products. Accordingly, the precursor used will generally not be the free acid, but a reactive derivative of the acid.

Suitable reactive derivatives include esters, typically lower alkyl, particularly C₁ to C₁₀ alkyl, esters. Thus, compounds of the formula (Ib) can be made by reacting an amine of the formula (II) above with an ester of the formula (V):



- 5 where R¹⁰, R¹¹, m and p are as defined above for formula (IIIb) and R¹² is a lower, particularly a C₁ to C₁₀, alkyl group, with the alcohol liberated typically being removed by distillation. The amidation reaction will typically be carried out at elevated temperatures e.g. 100 to 130°C e.g. when the group R¹² is a butyl group from 115 to 120°C, usually under an inert atmosphere e.g. nitrogen, optionally with a solvent or diluent e.g. using the alcohol R¹²OH as a diluent or
- 10 solvent, and will usually be carried out using a catalyst such as a transition metal alkoxide, particularly a titanium alkoxides e.g. titanium butoxide, a metal alkoxide e.g. sodium or potassium methoxide, or an alkali metal carbonate e.g. potassium carbonate. The temperature of the amidation reaction will generally be kept below about 150°C to avoid both decomposition of the usually sugar derived hydrophile group(s) in the amine (II) and trans-esterification reactions
- 15 catalysed by the amidation catalyst, but typically at temperatures above 100°C.

- The intermediate ester of the formula (V) can be made by reaction between the polyester acid of the formula (IIIb) and an alcohol R¹²OH, typically at elevated temperatures e.g. 80 to 200°C, usually under an inert atmosphere e.g. nitrogen, optionally with a solvent or diluent e.g. excess alcohol R¹²OH (which can be removed by distillation in the subsequent step), and will usually be
- 20 carried out using an acid catalyst, particularly a Lewis acid catalyst such as transition metal alkoxides e.g. titanium butoxide, or a heterogeneous acid catalyst such as an acidic ion exchange resin so that the catalyst can be readily separated from the reaction products e.g. by filtration, at the end of the reaction.

- When the polyester group is derived largely from relatively long chain hydroxy fatty acid residues particularly residues containing 12 or more carbon atoms e.g. 14 or more and especially 18 carbon
- 25 atoms, the group R¹² is, within the range C₁ to C₁₀, desirably a relatively long chain group, particularly containing 3 or more and especially 6 or more, carbon atoms, to aid synthesis of the intermediate ester. Using propyl or higher alcohols as a reaction medium enables the dissolution of the precursor polyester to give a homogeneous reaction, and using hexyl or higher alcohols can
- 30 aid ester synthesis by enabling ready separation of alcohol and water in the azeotropic distillate permitting ready return of the alcohol to the reaction mixture. Such esterifications are typically carried out at elevated temperature particularly close to the azeotropic reflux temperature which depends on the alcohol used.

- When the polyester group is derived largely from relatively short chain hydroxy fatty acid residues particularly residues containing 8 or fewer, particularly 5 to 7 and especially 6, carbon atoms, the
- 35

group R^{12} is, within the range C_1 to C_{10} , desirably a relatively short chain group e.g. a methyl, ethyl or propyl group. The polyesters derived from such acids tend to be soluble in relatively short chain alcohols and the lower boiling point of such alcohols makes it easier to remove them in the subsequent amidation step.

- 5 When the polyester combines both relatively short and long chain hydroxyl fatty acids, the particular alcohol used to form the intermediate ester and the reaction conditions will generally be chosen within the practical considerations set out above.

Where the precursor of the polyester is a lactone, such as polycaprolactone, various synthetic possibilities are available, because the polymerisation reaction leading to the polyester does not co-generate water. Thus, the reactive derivative of the polyester can be made by

- 10 i reacting the lactone initially with a fatty acid $R^{10}COOH$, where R^{10} is as defined above in formula (IIIb), but usually a relatively short chain, e.g. a C_2 to C_{10} fatty acid, and using this ester as a starting molecule for the polyesterification reaction (on the $COOH$ functionality freed by the lactone ring opening) and subsequently forming an ester of the polyester with an
- 15 alcohol $R^{12}OH$; or
- ii reacting the lactone initially with an alcohol, $R^{12}OH$, typically a relatively short chain, particularly a C_1 to C_6 alcohol, using this ester as a starting molecule for the polyesterification reaction (on the OH functionality freed by the lactone ring opening) to give an R^{12} ester of the polyester.
- 20 Such polyesterification reactions using lactones are typically carried out at elevated temperature particularly from 80 to 150°C and may use a catalyst, particularly a transition metal alkoxide or *p*-toluene sulphonic acid.

Another possible reaction sequence using lactone reagents, such as caprolactone, is to make an amide by reaction of the lactone with an amine of the formula (II), to give a monomeric hydroxy acid amide, and polymerising the polyester chain on the free OH group. This reaction may be

25 carried out as a two step reaction or as a single step reaction relying on the reactivity of the amine to make the amide before chain extension polymerisation becomes the major reaction. This sequence will typically be catalysed with a transition metal alkoxide, organoacid or acidic ion exchange medium catalyst. With this sequence, care will usually be needed to avoid the lactone

30 forming polyester chains based on the hydroxyl groups of the hydrophile group attached to the amido nitrogen atom.

As is mentioned above the surfactants of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) are useful as water in oil emulsifiers and/or stabilisers, as emulsifiers/stabilisers for certain types of water in oil emulsion and as dispersants for solids in

35 liquids, aqueous and non-aqueous. As such they can be used in a wide variety of applications

including in (water in oil) emulsion polymerisations, particularly the manufacture of polyacrylamide (PAM) and related polymers by the inverse emulsion polymerisation (i-PAM) method; in emulsion explosives; in cosmetic emulsions (for example in the general types of emulsion described in published PCT Application WO 98/55088 A); in agrochemical, particularly plant growth regulator, herbicide, and/or pesticides, emulsions and suspoemulsions, and as emulsifiers and/or dispersants; for dispersions of solids, such as pigments and/or inert inorganic metal salts, especially in organic media; as oil field drilling fluid additives, particularly as dispersants and/or emulsifiers for drilling muds and invert emulsion drilling fluids; and in metal working applications particularly in rolling oil emulsions and cutting fluids.

- 10 The invention accordingly includes the use of surfactants of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) as water in oil emulsifiers and/or stabilisers, as emulsifiers/stabilisers for water in oil emulsion and as dispersants for solids in aqueous or non-aqueous liquids.

The polymeric surfactants of the invention can be used as emulsifiers in making polyacrylamide. Typically, PAM is made by so-called inverse emulsion polymerisation, which is usually a free radical initiated polymerisation in which acrylamide, with any co-monomer(s), are dissolved in water, this solution is emulsified in an oil and the polymerisation initiated, typically by raising the temperature (with polymerisation initiator present) or by adding polymerisation initiator. The water in oil emulsion is typically emulsified and stabilised by a surfactant system. At the end of polymerisation the system is a dispersion of water droplets, containing dissolved PAM, in the oil phase. Although the viscosity of the aqueous PAM solution is high, the effective viscosity of the emulsion is determined primarily by that of the oil continuous phase and this is chosen to be suitably low. To introduce the PAM effectively into the typically aqueous systems in which it is to be used, the emulsion has to be broken. Typically, the system is designed so that it undergoes inversion on simple dilution into water. This general type of synthetic method is usually referred to as inverse polyacrylamide emulsion polymerisation, commonly abbreviated to "i-PAM". The requirements for the surfactant system used in inverse PAM polymerisation are thus somewhat unusual because it must provide adequate emulsion stability before, during and after (for storage) the polymerisation reaction, but must permit ready breaking of the emulsion during inversion on dilution into water, to facilitate rapid release of the polyacrylamide polymer into the water phase in which it will act. Inversion is commonly promoted by the addition of hydrophilic surfactants after completion of the polymerisation. The polymeric surfactants of the invention can be used to emulsify and/or stabilise the water in oil emulsion used in this type of polymerisation process.

The invention accordingly includes a method of making polyacrylamide by inverse emulsion polymerisation which comprises dispersing an aqueous solution of polymerisable monomers

including acrylamide in an oil phase the system also including a water in oil surfactant including at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) and polymerising the polymerisable monomers to form a colloidal suspension of particles, of a solution or dispersion of the resulting polyacrylamide polymer in water,
5 in the oil.

In this aspect of the invention, the oil phase may be a mineral oil, specifically a hydrocarbon, and particularly a paraffin, oil and especially an isoparaffin oil, or an ester oil as is described in published PCT Application No WO 98/09998 A. The amount of emulsifier surfactant used will typically be from 2.5 to 7%, more usually from 3 to 4%, by weight of the polymerisation emulsion.
10 Commonly, the emulsifier will be a combination of a polymeric surfactant, particularly including a surfactant of the formula (I), and a low molecular weight low HLB surfactant, which is used to prevent the stabilisation of the emulsion being so good that inversion is made difficult, because it is relatively less effective as an emulsion stabiliser and its low molecular weight means that it can readily diffuse away from the phase interface during inversion. Commonly such surfactants are
15 fatty acid monoglycerides, fatty acid sorbitan esters or similar surfactants. The relative proportions by weight of polymeric surfactant to low HLB low molecular weight surfactant is typically from 5:95 to 50:50 more usually from 10:90 to 40:60 and commonly about 15:85 to 30:70. The emulsifiers of the formula (I) can be used alone or in combination with other polymeric emulsifiers, but desirably, the proportion of emulsifier of the formula (I) is at least 50%, more usually at least 75%, by weight
20 of the total emulsifier used in stabilising the polymerisation emulsion.

The polyacrylamide (co)polymers made by such methods find typical use in water treatment particularly by being diluted and inverted into water thus liberating the (co)polyacrylamide as an aqueous solution that dilutes readily in the bulk aqueous phase. As is known in this art relatively hydrophilic surfactants, particularly oil in water emulsifiers having a high HLB e.g. above 12, will
25 usually be added to the water in oil inverse emulsion containing the polymer before dilution in the bulk aqueous phase to improve the speed and overall extent of inversion and liberation of the co(polyacrylamide) into the bulk aqueous phase.

Thus in this aspect the invention further includes a method of water treatment that includes diluting an inverse polyacrylamide emulsion, made by the method of this aspect of the invention into the
30 water to be treated such that the emulsion is inverted releasing the polyacrylamide into the water and emulsifying the oil phase in the dilution water.

The polymeric surfactants of the invention are also useful in making emulsion explosives. Emulsion explosives typically use a combination of a fuel and an oxidiser, which are emulsified to bring them into intimate contact. Usually, the oxidiser is an aqueous solution of an oxidiser salt
35 solution, most commonly based on ammonium nitrate, which is dispersed as fine droplets in a

- liquid fuel phase. The fuel is typically a hydrocarbon fuel such as mineral and/or paraffin oil, which may also include straight and/or branched chain waxes such as micro-crystalline wax, paraffin wax and slack wax, and/or petroleum refining distillation residues such as LSHS (low sulphur heavy stock). The oxidiser is usually an aqueous solution, commonly a saturated or supersaturated
- 5 solution, of nitrate salts, particularly NH_4NO_3 , alkali metal nitrates such as NaNO_3 and/or KNO_3 or alkaline earth metal nitrates such as $\text{Ca}(\text{NO}_3)_2$, and may include minor proportions of other salts such as NH_4Cl . Typically, the oxidiser phase contains from 40% to 70% by weight of ammonium nitrate and 20% of other nitrates dissolved in water, which is typically from about 5 to about 16% by weight of the oxidiser phase. The internal oxidiser phase is typically at least 75% more usually
- 10 more than 90% e.g. about 95%, by volume of the emulsion explosive. For use, emulsion explosives typically also include additives to sensitise the compositions to detonation. Commonly this is done by adding materials that provide solid surfaces e.g. solid NH_4NO_3 , especially as prills, or gas filled voids e.g. by including sodium nitrite, which produces gas by chemical reaction, or glass microspheres, which provide physical voids.
- 15 Emulsion explosives are usually stabilised (against phase separation) by an emulsifier, which is typically an oil soluble emulsifier. The surfactants of this invention have shown promise as emulsifiers for emulsion explosives and the invention accordingly includes an emulsion explosive in which an aqueous phase including an oxidiser is emulsified in a fuel phase and in which at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as
- 20 defined above) is included as an emulsifier for the aqueous phase. The emulsifiers of the formula (I) can be used alone or in combination with other typically oil soluble emulsifiers particularly sorbitan fatty acid esters such as sorbitan mono oleate (SMO); phospholipids such as soyalecithin or oxazoline or imidazoline derivatives thereof; PIBSA alkanolamine reaction products; condensation products of fatty acids with polyethylene glycol of various molecular weight. The total
- 25 amount of emulsifier used in emulsion explosives in this aspect of the invention is typically from 0.5 to 5%, more usually from 1 to 4%, by weight based on the overall emulsion. Desirably, the proportion of emulsifier of the formula (I) is at least 50%, more usually at least 75%, by weight of the total emulsifier used in the emulsion explosive.
- Further this aspect of the invention includes a method of causing explosions, particularly for
- 30 excavation, particularly quarrying or mining, which method includes introducing an emulsion explosive of the invention into a rock formation and subsequently detonating the explosive.
- The polymeric surfactants of the invention can be used as water in oil dispersants and/or emulsifiers in personal care and cosmetic applications. In particular, the surfactants are useful in formulations including relatively high concentrations of solutes in a dispersed hydrophilic phase and
- 35 in the manufacture of multiple emulsions.

Accordingly the invention includes a personal care composition which is or includes an aqueous phase dispersed or emulsified in an oil phase which includes as a dispersant and/or emulsifying agent at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above).

- 5 The oil phase used in this aspect of the invention is typically an emollient oil which may be liquid or solid at ambient temperature. Suitable liquid emollient oils include non-polar oils such as mineral oils e.g. paraffin or *iso*-paraffin oils, and polar oils, particularly ester oils such as triglyceride oil e.g. vegetable oils or synthetic triglycerides, synthetic ester oils, ether oils, silicone oils and alkoxylated oils. Suitable emollients that are solid at ambient temperature include emollient waxes such as
- 10 paraffin waxes, ozokerite, beeswax and vegetable waxes e.g. castor wax and candelilla wax. The oil phase may be a mixture or blends of more than one emollient oil and/or wax and may include other components such as essential oils, oil soluble vitamins, antioxidants, pigments, hydrophobic silica (such as Aerosil R972 ex Degussa), UVB and UVA sunscreen agents (see also below), and similar materials. The volume proportion of the emollient oil continuous phase is typically from 5%
- 15 to 95%, more usually from 10 to 50%, by weight of the overall emulsion.

- The discontinuous, usually aqueous, phase can be water or a water based liquid, or a hydrophilic phase which can be a solution in water of the hydrophilic material or the discontinuous phase can, in certain cases, be a substantially water free liquid phase of the hydrophilic material. Thus, the invention includes a personal care composition which is or includes an emulsion or dispersions of a
- 20 hydrophilic phase in an oil continuous phase which further includes as a dispersant and/or emulsifying agent an amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above).

In this aspect the invention includes :

- 1 a personal care composition which is or includes a water in oil emulsion or dispersion in
- 25 which the dispersed water phase includes dissolved therein at least one electrolyte, particularly where the electrolyte is aluminium and/or zirconium chlorohydrate, sodium chloride or a salt of an organic acids such as sodium lactate, and particularly at a concentration of from 0.1 to 25% by weight of the aqueous phase, and which further includes as a dispersant and/or emulsifying agent an amide surfactant compound of the formula (I),
- 30 and specifically of the formulae (Ia) and (Ib), (as defined above);
- 2 a personal care composition which is or includes a water-in-oil emulsion or dispersion in which the dispersed water phase includes urea dissolved therein, particularly at a concentration of from 0.1 to 20% by weight of the aqueous phase, and which further includes as a dispersant and/or emulsifying agent an amide surfactant compound of the formula (I),
- 35 and specifically of the formulae (Ia) and (Ib), (as defined above);

- 3 a personal care composition which is or includes a hydrophile in oil emulsion or dispersion in which the dispersed hydrophile phase is a polyol or is water having a polyol dissolved therein, particularly glycerol, glycerol ethoxylated with from 1 to 100 moles of ethylene oxide, propylene, butylene and/or hexylene glycol, sorbitol, sorbitol ethoxylated with from 1 to 100
5 moles of ethylene oxide and polyethylene glycol (especially having a molecular weight distribution between 200 to 6000 Daltons (Da) with a typical average molecular weight of about 1500 Da), and which further includes as a dispersant and/or emulsifying agent an amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above); and
- 10 4 a personal care composition which is or includes a water in oil emulsion or dispersion in which the dispersed water phase includes at least one alcohol dissolved therein, particularly in an amount of from 1 to 40%, and which further includes as a dispersant and/or emulsifying agent an amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above).

- 15 In such systems the surfactant of the invention is typically used in an amount of 0.5 to 5%, more usually from 1 to 2%, by weight of the total emulsion.

Particularly for the hydrophile in oil emulsion (possibility 3 above) the system can be formulated as a multiple water in oil in water emulsion, by dispersing a water, particularly hydrophile, in oil emulsion in an aqueous phase, usually water, i.e. using conventional 2-step multiple emulsion
20 manufacturing methods. Such double emulsions can contain from 30 to 90%, particularly from 50 to 80%, by weight based on the total multiple emulsion of the primary internal phase. Where the hydrophile is a glycol or, and particularly, glycerol, the hydrophile phase may contain little if any water. This opens the possibility of making aqueous emulsions containing water sensitive materials, or materials that are sensitive to other environmental effects e.g. oxidation, in the
25 presence of water, such as some water soluble vitamins especially vitamin C. The water sensitive material is dissolved in the hydrophile phase emulsified in an oil continuous phase and this emulsion is then emulsified into water or an aqueous phase.

The invention further includes a method of making an oil in water cosmetic or personal care emulsion containing water in oil droplets which includes forming a mixture of an oil phase and oil in
30 water primary emulsifier for dispersing oil in an aqueous phase including also an amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above), and adding to the oil mixture under stirring to an aqueous phase.

One area of practical importance in this aspect of the invention is sunfilters and sunscreens or other cosmetics containing sunfilter and/or sunscreen components. The sunfilters or sunscreens
35 can be physical sunscreens such as those based on titanium dioxide e.g. ultra-fine titanium

dioxide, or zinc oxide, which are understood to act by strongly scattering ultraviolet radiation, or chemical sunfilters or sunscreens such as compounds that absorb ultraviolet radiation, particularly UVB and UVA sunscreen agents. The amount of sunfilters and/or sunscreen used will depend on the properties of the materials used, but typically for physical sunscreens the amount will be 0.1% to 5%, more usually from 0.25 to 2.5%, by weight of the overall emulsion and for chemical sunfilters and/or sunscreens 0.05 to 3%, more usually from 0.1 to 1.5%, by weight of the overall emulsion. Depending on their nature the sunfilter and sunscreen components may be present in the generally aqueous discontinuous phase or in the oil continuous phase or in both phases. Particularly where the sunscreens is a physical sunscreen, the overall emulsion will be combined suspension and emulsion and these are commonly referred to as suspoemulsions (see further below).

Suspoemulsions are a further important area in this aspect of the invention. They are briefly referred to above in connection with sunscreens, but other solid components can be included such as pigments as are often included in make up cosmetics. When pigments are used, they may be pigments organic or inorganic and may be present in the oil phase, particularly for organic pigments and hydrophobic inorganic pigments, or in the present in the water phase, particularly for hydrophilic inorganic pigments, or in both phases, when used are typically present in concentrations of from 0.5 to 20% more usually from 1 to 10%, by weight of the emulsion.

Generally the amount of the surfactant of the formula (I) used in cosmetic compositions of this aspect of the invention is from 0.5 to 7%, more usually from 1 to 5%, by weight of the formulation. The emulsifiers of the formula (I) can be used alone or in combination with other polymeric emulsifiers, but desirably, the proportion of emulsifier of the formula (I) is at least 50%, more usually at least 75%, by weight of the total emulsifier used in stabilising the cosmetic emulsion.

In addition to the components mentioned above the emulsions of this aspect of the invention can include other components. Examples include:

preservatives such as those based on parabens (alkyl esters of 4-hydroxybenzoic acid), phenoxyethanol, substituted ureas and hydantoin derivatives e.g. those sold commercially under the trade names Germaben II Nipaguard BPX and Nipaguard DMDMH, when used usually in a concentration of from 0.5 to 2% by weight of the emulsion; perfumes, when used typically at a concentration of from 0.1 to 10% more usually up to about 5% and particularly up to about 2% by weight of the emulsion.

The polymeric surfactants of the invention can further be used as dispersants for the production of dispersions of finely divided solids of various types in fluids and particularly in liquid organic media. Accordingly, the present invention provides a dispersion of a solid in a liquid phase, particularly an organic liquid phase which includes as a dispersant at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above).

Examples of materials that can be dispersed in such applications include pigments, particularly for paints and solvent inks, such as described in the Colour Index (3rd Ed 1971) under 'Pigments'; dyes including disperse dyes; magnetic metal oxides; extenders and fillers e.g. for paints and plastics materials; optical brightening agents; and textile auxiliaries, particularly for solvent dye baths; solids for oil based and invert emulsion drilling muds; dirt and solid particles in dry cleaning fluids; magnetic materials for magnetic recording media; and agrochemicals such as fungicides (see also below concerning agrochemical applications). The medium is typically an oil such as a hydrocarbon oil or an ester oil, which may be natural or synthetic, or a coating composition resin such as an alkyd resin, or special mixture of glycols typically used in the preparation of so-called multi-purpose pigment pastes or pigment concentrates.

Such dispersions typically contain from 5 to 95%, more usually from 10 to 60%, and especially from 20 to 50%, by weight of the solid, the precise quantity depending on the nature of the solid and the relative densities. The dispersion may be made by conventional method for making dispersions. Thus, the solid, the usually organic medium and the dispersant may be mixed in any suitable order and the mixture can then be subjected to mechanical treatment e.g. grinding or milling, to reduce the particles of the solid to an appropriate size and/or to suspend or disperse the solid particles in the medium.

The amount of dispersant used in this kind of application will typically be from 10 to 90%, more usually from 15 to 65% by weight of the pigment. The surfactants of the formula (I) can be used alone or in combination with other polymeric surfactants, but desirably, the proportion of surfactant of the formula (I) is at least 50%, more usually at least 75%, by weight of the total surfactant used in stabilising the dispersion.

The polymeric surfactants of this invention can be used in various forms of emulsion and dispersion in agrochemical applications. The invention accordingly includes an agrochemical emulsion or dispersion, in which at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) is included as an emulsifier or dispersant. Within this, more particularly the invention includes:

- i an agrochemical emulsion including an agrochemically active material which is dissolved, dispersed or emulsified in a first liquid component, the first liquid component being emulsified in a second liquid component;
- ii an agrochemical formulation including an agrochemically active material which is dissolved, dispersed or emulsified in a first liquid component, a second liquid component being emulsified in the first liquid component;
- iii an agrochemical dispersion in which a solid component is dispersed in a liquid phase.

The agrochemically active material(s) included in the emulsions and/or dispersions in this aspect of the invention can include one or more plant growth regulators, herbicides, and/or pesticides, for example insecticides, fungicides, acaricides, nematocides, miticides, rodenticides, bactericides, molluscicides and bird repellants. Examples of classes of actives include:

- 5 Herbicides: including water soluble, particularly non-selective, herbicides, particularly *N*-phosphonomethyl glycine herbicides e.g. Glyphosate and Sulfosate, and the glufosinate and bipyridyl types of non-selective herbicides, triazines, substituted ureas, sulphonyl ureas, pyridine carboxylic acids, aryloxy alkanoic acids, 2-(4-aryloxy-phenoxy)propionic acids, bis-carbamates;
- 10 Fungicides: including thiocarbamates, particularly alkylenebis(dithiocarbamate)s, strobilurins, dicarboximides, benzimidazoles, azoles, inorganic fungicides;
- Insecticides including benzoyl ureas and
- Acaricides including tetrazines.

Particular applications of the polymeric surfactants of the invention in agrochemicals include:

- 15 Concentrated emulsions which contain both aqueous and non-aqueous phases with the continuous phase usually being aqueous. They are increasing in popularity because they provide reduced flammability, reduced solvent requirements, lower skin and eye irritation, and the ability to combine water and oil soluble actives and inerts. The proportion of polymeric emulsifier is typically from 0.1 to 15%, more usually from 0.5 to 1.5% by weight of the
- 20 emulsion.

- Oil in water agrochemical emulsions are generally non-transparent white emulsions which are applied after further dilution in the spray tank. The internal phase is typically a solvent with dissolved active ingredient, while the external phase is typically aqueous and may include other water soluble components such as anti-freeze, preservative, dye, adjuvant, fertiliser
- 25 and/or other actives. Oil in water emulsions can be emulsified either by using the polymeric surfactants of the invention alone, in which case they will typically be used at from 3 to 8%, particularly about 5%, by weight of polymeric emulsifier based on the emulsion; or they can be used, particularly to enhance stability, in combination with a relatively hydrophilic surfactant e.g. one having an HLB value of 10 or more e.g. a hydrophilic alcohol alkoxylate.
- 30 In this case, the proportion of polymeric emulsifier is typically from 0.1 to 10%, more usually from 3 to 8% and commonly about 5%, by weight of polymeric emulsifier based on the emulsion.

- Water in oil emulsions are generally non-transparent white emulsions. They are typically commercialised as ready to use formulations, ultra low volume systems, and other specialty
- 35 applications. The external oil typically serves as carrier for the active ingredient as well as aiding the spreading and penetration of the active. The emulsion is usually sprayed as such

on the target. The proportion of polymeric emulsifier is typically from 1 to 15%, more usually from 3 to 8% and commonly about 5%, by weight of polymeric emulsifier based on the emulsion.

Dispersions, in an aqueous or oil based liquid, of solid components which commonly will be

5 insoluble actives, particularly fungicides or herbicides, but may be non-agrochemically active insoluble solid components. In oil based formulations, the polymeric surfactant will commonly be used alone, typically at from 2 to 8%, more usually from 2 to 5%, by weight of the dispersion. In water based formulations, a wetting agent e.g. an alcohol alkoxylates wetting agent, will usually be included commonly at from 1 to 5%, more usually from 2 to 3%,
10 by weight of the dispersion, with the polymeric surfactant at from 1 to 5%, by weight of the dispersion. Such dispersions, particularly the oil based dispersions, may be incorporated into suspoemulsions (see below).

Suspoemulsions which are systems in which at least one liquid and at least one solid disperse

15 phase is included in a continuous phase, which is usually aqueous. They are particularly suitable for agrochemical formulations which include an oil soluble active and a solid water insoluble (and usually also oil insoluble) active, with the oil soluble active present as an emulsion and the solid water insoluble active present as dispersed particles. The dispersed phase may itself be dispersed within the oil based emulsion droplets. The proportion of polymeric emulsifier is typically from 0.1 to 10%, more usually from 0.5 to 1.5% by weight of
20 the emulsion. Suspoemulsions will commonly include relatively hydrophilic surfactant e.g. one having an HLB value of 10 or more such as a hydrophilic alcohol alkoxylate, or an anionic surfactant, typically used at from 1 to 10%, more usually from 3 to 5%, by weight of the suspoemulsion, to aid emulsification of the oil disperse phase in the (usually) aqueous continuous phase.

25 In these agrochemical applications, the emulsions and/or dispersions can include other particularly surfactants such as:

anionic surfactants e.g. alkali metal or alkali earth metal salts of sulphonated hydrocarbons such as alkyl benzene sulphonates particularly Ca dodecylbenzene sulphonate, typically included at from 0.1 to 10%, more usually from 2 to 3%, by weight of the emulsion; and/or

30 alcohol alkoxylates such as those based on C₈ to C₂₂, particularly C₁₂ to C₁₈, alcohols, which may have straight or branched, usually alkyl, chains, and which are alkoxylated with ethylene oxide, propylene oxide or copolymeric chains including residues of both ethylene oxide and propylene oxide, which may be block or random (statistical) copolymeric chains, commercially available examples include: Atlas G-5000, Atlox MBA 1306 and Synperonic
35 A11/A20 available from Uniqema. Alcohol alkoxylates are typically included at from 0.1 to 10%, more usually from 2 to 3%, by weight of the emulsion.

In agrochemical compositions, the surfactants of the formula (I) can be used alone or in combination with other polymeric surfactants, but desirably, the proportion of surfactant of the formula (I) is at least 50%, more usually at least 75%, by weight of the total polymeric surfactant used as an emulsifier and/or stabiliser in the composition.

- 5 The polymeric surfactants of the invention can be used in oilfield applications such as oil drilling mud dispersants and as water in oil emulsifiers in invert drilling fluids.

In oil drilling muds, the fluid carrier is typically aqueous, and may be a brine, typically including NaCl, CaCl₂, MgCl and/or ZnBr at a concentration, depending on the desired overall density of the mud, up to saturation. Mud also includes particulate solid weighting agents, to increase the
10 overall density of the fluid to help balance well bottom pressure. Suitable weighting agents include barite, iron oxides such as haematite, and ilmenite. The proportion of weighting agent depends on the overall desired density, but is typically from 5 to 90% by weight of the mud. Drilling muds may also include emulsified oils, such as hydrocarbon oils, particularly petroleum fractions such as kerosene and diesel oil, mineral oils and vegetable oils, typically at from 1 to 20% by weight of the
15 mud, and additives such as emulsifiers (for emulsified oil), fluid loss agents and viscosifiers depending upon the particular drilling activity.

The polymeric surfactants of the invention can be used in drilling muds to aid dispersion of weighting agents, particularly to inhibit sedimentation when drilling is stopped. The invention accordingly includes an oil drilling mud which is a dispersion of a weighting agent in an aqueous
20 liquid phase which includes as a dispersant at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above). In drilling muds, the proportion of polymeric dispersing surfactant is influenced by the desired mud density, the nature of the weighting agent particularly its density, particle size distribution and surface characteristics, and the proportion present, but is typically from 0.5 to 10%, more usually from 1 to 7%, by weight of the
25 mud. The dispersants of the formula (I) can be used alone or in combination with other polymeric dispersants, but desirably, the proportion of dispersant of the formula (I) is at least 50%, more usually at least 75%, by weight of the total dispersant used in stabilising the dispersion.

The surfactants of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) can also be used as emulsifiers and/or dispersants in invert drilling fluids and accordingly the
30 invention further includes an invert drilling fluid which is an emulsion of an aqueous, particularly a brine, phase in an oil, which fluid optionally further includes a dispersion of a weighting agent, which drilling fluid includes as an emulsifier and/or dispersant at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above).

Invert drilling fluids are water in oil emulsions with a fluid component which typically is made up of

from 90 to 10% by weight of oil phase and from 10 to 90% by weight aqueous phase. The aqueous phase is commonly a brine, usually a NaCl or CaCl₂ brine and the oil phase is commonly a mineral oil such as a hydrocarbon oil. The emulsion is stabilised using an emulsifying agent which is usually present at from 0.2 to 10%, more usually 1 to 7%, by weight of the aqueous phase.

- 5 Invert drilling fluids also usually include weighting agents and the surfactants of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above) can also be used as dispersants for the weighting agents, particularly to inhibit sedimentation when drilling is stopped. the weighting agent can be of the types mentioned above for drilling muds. The concentration of dispersing agent used is influenced by the desired mud density, the nature of the weighting agent particularly its density,
- 10 particle size distribution and surface characteristics, and the proportion present. Typically, the dispersing agent will be used an amount from 0.1 to 10% by weight of the weighting agent. Other components can include fluid loss agents and viscosifiers depending upon the particular drilling activity.

- In invert drilling fluids, the emulsifiers/dispersants of the formula (I) can be used alone or in
- 15 combination with other polymeric emulsifiers/dispersants, but desirably, the proportion of emulsifier of the formula (I) is at least 50%, more usually at least 75%, by weight of the total emulsifier/dispersant used in the invert drilling fluid.

The polymeric surfactants of this invention can also be used in lubricants and/or coolants in metal working applications particularly in metal forming applications and metal cutting operations.

- 20 Metal forming fluids provide lubrication in metal forming operations, particularly rolling, drawing and stamping. Rolling is the largest scale such operation and is generally representative of these operations and the application of the surfactants of the invention is described below in terms of rolling oils.

- Rolling oils are fluids that provide lubrication in metal rolling, particularly cold rolling, processes e.g.
- 25 cold rolling of steel sheet and tinplate. Typically, they are used as oil in water emulsions in which the lubricating oil is the discontinuous phase in an aqueous continuous phase. Commonly rolling oils are produced as concentrates which are usually solutions of the emulsifier (and any other additives) in the oil which emulsifies when diluted into water prior to use.

- The use of such polymeric surfactants enables rolling oil emulsions in which the oil droplet size is in
- 30 the typical range of 2 to 5 μm usually favoured for cold rolling steel sheet, or larger, typically from 6 to 15 μm , used in tinplate rolling. Particularly with larger droplet sizes, the polymeric surfactants can provide stability against undesired coalescence of the oil droplets even though the emulsion may be meta-stable in that reversible creaming of the oil phase may occur. Further, polymeric surfactants can give improved 'tramp oil' rejection, emulsion stability under high shear mixing, and,

better stability under extreme conditions such as high temperature, high electrolyte concentrations, and high internal phase volumes.

Rolling oil concentrates are typically emulsified into water at 2 to 3% oil in water for sheet rolling and 4 to 6% oil in water for tinplate rolling. The amount of polymeric surfactant used in rolling oil emulsions is typically from 0.1 to 2.0% by weight based on the rolling oil concentrate. The surfactants of the formula (I) will typically be used in combination with other surfactants such as alcohol ethoxylates, nonylphenol ethoxylates and/or EO/PO block copolymers, such that the total surfactant concentration is typically from 2 to 5% by weight of the oil component of the rolling oil, with the polymeric surfactant being typically from 10 to 40% of the total surfactant. The surfactants of the formula (I) may be used in combination with other polymeric surfactants, but will usually be at least 50% and more usually at least 75% of the total polymeric surfactant used in a rolling oil concentrate or emulsion.

Typically, rolling oil formulations are based on lubricants which are commonly blends of mineral oils e.g. paraffinic or naphthenic base oils, synthetic esters e.g. trimethylolpropane trioleate, neopentyl glycol cocoate, butyl stearate, and similar esters, natural oils and fats e.g. coconut oil, palm oil, tallow, and similar fats. they may include other additives such as load carrying additives e.g. sulphurised oils and phosphate esters; and antioxidants, dropping agents, antifoam additives, anticorrosive additives.

The invention accordingly includes a rolling oil emulsion which is an oil in water emulsion of a rolling oil which includes as an emulsifier at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above). The invention further includes a rolling oil concentrate which is a solution in a rolling oil of at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above), which solution is emulsifiable in water to form a rolling oil emulsion.

Water in oil emulsion rolling oils have been used for rolling stainless steel and the polymeric surfactants of this invention can be used in such formulations. In such applications the proportion of polymeric surfactant used is typically from 1 to 5%, more usually 2 to 3%, by weight of the total emulsion formulation.

Cutting fluids provide lubrication and cooling in metal working applications that involve removing metal from a workpiece, particularly operations such as drilling, lathe working, milling, grinding and parting.

There are several types of cutting oil in general use. The surfactants of the invention are particularly applicable in emulsion and/or microemulsion formulations. These include:

Soluble oils are typically formulated as concentrates which are homogeneous blends, usually

solutions or microemulsions, of an oil or a mixture of oils, a surfactant and optionally additives such as anticorrosion and/or extreme pressure additives, which are diluted with water to form an oil in water emulsion before use.

"semi synthetic" formulations which in use are oil in water micro-emulsions which are typically translucent or transparent and typically have an average oil droplet size of 500 nm (or less). They are typically formulated as concentrates and diluted with water before use. water in oil emulsions or microemulsions, which will usually be formulated to be used without dilution.

The invention accordingly includes a cutting fluid emulsion which is an emulsion, including an oil phase and an aqueous phase, which includes as an emulsifier and/or a stabiliser at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above). More particularly this aspect of the invention includes a cutting fluid emulsion which is an oil in water emulsion of an oil, which includes as an emulsifier at least one amide surfactant compound of the formula (I). The invention further includes a cutting fluid concentrate which is a solution in an oil phase of at least one amide surfactant compound of the formula (I), and specifically of the formulae (Ia) and (Ib), (as defined above), which solution is emulsifiable in water to form a cutting oil emulsion.

The oil used in the cutting oil can be from a wide variety of oils including hydrocarbon, particularly mineral, oils e.g. paraffinic or naphthenic base oils; ester oils, including natural glyceride oils e.g. coconut oil, palm oil or tallow; or synthetic esters e.g. trimethylolpropane trioleate, neopentyl glycol cocoate and butyl stearate. The proportion of oil in cutting fluid concentrates is typically from 5 to 50%, more usually from 10 to 30%, by weight of the concentrate.

The total surfactant levels in cutting oil formulations is typically from 10 to 60% by weight based on the oil phase, but usually 15 to 25% for soluble oil formulations and 25 to 50% for so-called semi-synthetic formulations. Typically the polymeric surfactant will be from 5 to 50%, more usually from 10 to 30% by weight of the total surfactant. For cutting fluids, the co-surfactants are typically blends of anionic surfactants such as sulphonates and/or carboxylates, and, nonionic surfactants such as alcohol alkoxyates, nonylphenol ethoxyates, alkanolamides and/or EO/PO block copolymers. In cutting oil formulations, the surfactants of the formula (I) may be used in combination with other polymeric surfactants, but will usually be at least 50% and more usually at least 75% of the total polymeric surfactant used in a rolling oil concentrate or emulsion.

Commonly cutting fluids, particularly the soluble oils and the so-called "semi-synthetic" types, are produced as concentrates which are usually solutions or microemulsions of the emulsifier (and any other additives) and usually some water in the oil which is diluted with water prior to use. Emulsion cutting fluid concentrates are typically diluted with water prior to use to give an oil content

depending on the end use duty. Typically, dilution is to an oil content of from 1 to 30%, more usually from 2 to 10%, by weight of the cutting oil emulsion.

Cutting oils may include functional additives such as extreme pressure and/or anticorrosion additives, typically at levels, when present, of from 1 to 10% of the oil phase in the cutting oil.

- 5 The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise stated.

Materials

- PIBSA polyisobutylene succinic anhydride
- PHSA polyhydroxystearic acid, Hypermer LP1 ex Uniqema
- 10 Pol1 Polymeric surfactant - PIBSA diethanolamine reaction product 80% active in non aromatic hydrocarbon solvent ex-Uniqema
- Pol2 Polymeric Surfactant - PHS-PEG-PHS block copolymer ex-Uniqema
- Pol3 Polymeric surfactant - PIBSA diethanolamine reaction product 85% active in xylene solvent ex-Uniqema
- 15 Span 80 sorbitan mono-oleate ex-Uniqema
- AM Acrylamide
- AA Acrylic acid
- DMAEM-MeCl 2-(dimethylamino)ethyl methacrylate quaternised with methyl chloride
- 20 AIBN α, α' -azoisobutyronitrile
- Isopar L C12/C13 isoparaffinic solvent; ex Exxon
- Water demineralised water
- NaOH 50% weight/volume aqueous solution
- HCl 37% weight/volume aqueous solution
- 25 EDTA 5% weight aqueous solution
- KBrO₃ 1.5% weight aqueous solution
- CuSO₄ 1% weight aqueous solution

Manufacturing and test methods

Emulsion explosives were made by the following (conventional) method at a 10 kg batch size.

- 30 Aqueous oxidiser phase was added gradually to the fuel phase in a Patterson mixer at a (vertical) speed of 300 rpm (5 Hz) over 5 to 6 minutes at 85°C. The mixing was continued for a further 20 minutes to achieve proper refinement of the emulsion droplets and to produce a flowable type of low viscosity emulsion.

Test Methods

Viscosity was measured at about the yield point of the emulsion using a Brookfield viscometer, spindle 7 at 1 rpm (ca 0.017 Hz) at 70°C, results are expressed in kPa.s (instrumentally the results are obtained as cP; 1kPa.s = 10⁵ cP)

- 5 Droplet size average droplet size was measured using a HORIBA particle size analyser (light scattering) and the results are quoted in µm.

- 10 The emulsions were sensitised using sodium nitrite and the explosive sensitivity was measured on a 32 mm diameter test cartridge using a no 6 copper electric detonator (CED-6). Sensitivity after storage was assessed as Yes/No (Pass/Fail) and the velocity of detonation (VoD) was measured and is quoted in km.s⁻¹.

Emulsion (co)polymerisation of acrylamide (inverse polyacrylamide polymerisation) were carried out in a 500 ml Pyrex reactor fitted with a Teflon blade stirrer, a Pt 100 thermometer, a cooling loop (water flow control through electronically driven valves), a nitrogen inlet and an initiator inlet (fed by a Razel model A-99 syringe pump for addition of the reductant part of redox initiator).

15 Production procedure:

a) Polymerisation using water soluble redox initiator:

- 1 Purge aqueous phase and oil phase separately with nitrogen for 20 minutes.
- 2 Add oil phase in mixing beaker.
- 3 Add slowly aqueous phase while mixing with Silverson high shear mixer under continuous nitrogen purging.
- 20 4 Mix for 4 minutes at maximum speed setting on mixer.
- 5 Transfer the pre-emulsion into the reaction vessel and purge 20 minutes with nitrogen whilst stirring at 250 rpm.
- 6 The polymerisation start conditions were: water bath temperature : 50±1°C; reaction
- 25 temperature: 45±1°C; stirrer speed : 800 rpm (ca 13 Hz)
- 7 Start initiator feed (10 ml of 0.15% Na₂S₂O₅ in demineralised water for 500 g emulsion, added over a period of ca 4 hours).
- 8 After addition of all the initiator excess initiator (4 ml of 15% Na₂S₂O₅ in demineralised water for 500 g emulsion, over ca 30 minutes) was added to ensure complete polymerisation of the
- 30 monomer.
- 9 Determine the amount of coagulum.

b) Polymerisation using oil soluble, dissociative initiator (AIBN)

A similar procedure was used, except that step 7 and 8 were replaced by:

- 7 Add all initiator (1 ml of 16.7 wt% solution of AIBN in acetone for 500 g emulsion) in one lot,
- 35 when the temperature of the pre-emulsion reaches 40°C ± 1.

8 Polymerise for 6 hours under nitrogen purge.

Test methods

Coagulum content was assessed by

- 1 weighing the cooling loop and the N₂-inlet before and after polymerisation.
- 5 2 filtering the product emulsion on a 80 µm polypropylene filter and weighing the (wet) coagulum retained on the filter and the filtrate and calculating the percentage coagulum.

Synthesis Examples

Synthesis Example SE1

- 10 A heterogeneous mixture of 84.67 g N-methylglucamine (NMG), 415 g PIBSA and 500 g paraffin oil solvent was heated under stirring until the glucamine melted to give a liquid biphasic mixture (ca 130 to 140°C) and stirring was continued to give a clear homogeneous solution after ca 15 to 30 minutes. The reaction was then monitored by infra-red spectroscopy and after stirring for ca 2 hour, the mixture was cooled to give 1000 g of a wine red sticky liquid.

15 Synthesis Example SE2

- Amberlyst-15 (30 g, 5 wt% of total reaction mix) was added to a single phase mixture of PHSA (200 g) and n-butanol (400 g) and the mix was heated to reflux and the water of reaction was removed azeotropically. The reaction was monitored by acid value which stabilised after 4 hours. The reaction mixture was filtered to remove the catalyst and the filtrate was used directly for the
20 next step.

- N-methylglucamine (16 g; 0.082 mol) and K₂CO₃ (0.34 g; 0.00246 mol; 3 mol% of NMG used) were added to the clear solution of PHS butyl ester in butanol obtained by the previous step, and the mixture was refluxed. The NMG was completely dissolved after 1 hour. The reaction was then monitored initially by IR for the formation of amide carbonyl at 1620 cm⁻¹ and then by TLC for the
25 disappearance of NMG (or by following the reduction in acid number). The reaction was complete after a total reaction time of 5 hours. Removing butanol by distillation at reduced pressure gave the product as a brown viscous liquid.

Application Examples

Application Examples AE1a and AE1b illustrate emulsion explosives

30 Application Example AE1a

This Example illustrates the use of polymeric surfactants of the invention in the making and use of emulsion explosives. Emulsions were made up containing the following materials

	Material	Amount (wt parts)
Oil phase	SE1	3.00
	SMO	0.20
	Paraffin oil	0.80
	Microcrystalline wax	1.00
	Paraffin wax	1.00
Oxidiser phase	Aqueous NH_4NO_3 + small amount NaNO_3	94.00

A water-in-oil emulsion explosive composition was made as described above and test results are given in Table 1 below. The tests included sensitivity tests, fresh after making the cartridges and after 1 month, 3 months and 6 months storage under ambient conditions.

Application Example AE1b

- 5 An emulsion explosive was made and tested as described in Application Example AE1a but using the following formulation, including a reduced amount of emulsifier:

	Material	Amount (wt parts)
Oil phase	SE1	1.30
	Pol1	1.20
	SMO	0.50
	Paraffin oil	0.40
	Microcrystalline wax	1.30
	Paraffin wax	1.30
Oxidiser phase	Aqueous NH_4NO_3 + small amount NaNO_3	94.00

Test results are included in Table 1.

For comparison, an emulsion explosive was made up using Pol1 polymeric surfactant using an emulsions similar to that used in Example AE1a. The particle size and viscosity of this emulsion are included in Table 1 below.

10

Table 1 - Emulsion Explosive Test Results

Ex No	viscosity (kPa.s)	droplet size (mm)	Explosive testing		
			Storage	Sensitivity	VoD (km.s^{-1})
AE1a	20.00	4.00	fresh	Pass	2.50
			1 month	Pass	2.30
			3 months	Pass	2.30
AE1b	13.90	3.40			
AEC1	21.20	4.10			

Application Examples AE2a and AE2b illustrate emulsion polymerisation (inverse polyacrylamide polymerisation).

Application Example AE2a

This example illustrates inverse polyacrylamide polymerisation using surfactants of the invention as a component of the primary emulsifier. The emulsion polymerisation procedure described above using an oil soluble, dissociative catalyst was used to make an anionic polyacrylamide. The composition of the aqueous polymerisation (internal) phase was:

	Acrylamide	135.0 g
	Acrylic acid	58.0 g
10	Water	179.0 g
	NaOH (50% aqueous solution)	55.0 g
	EDTA (5% aqueous solution)	5.2 g
	the external phase was Isopar L	168.0 g
	and the amount of primary emulsifier	10.0 g

15 The primary emulsifier used was a mixture of surfactant of the invention, the compounds of SE nos 1 and 2, and a low HLB surfactant (Span 80). The polymerisation initiator used was AIBN and the reaction procedure described above for oil soluble, dissociative initiators was used. Comparative runs were carried out using conventional polymeric surfactants with the low HLB surfactant. The coagulum levels are given in Table 2 below.

20 Application Example AE2b

This illustrates inverse polyacrylamide polymerisation making a cationic polyacrylamide. The composition of the aqueous polymerisation (internal) phase was:

	Acrylamide	96.5 g
	DMAEM MeCl	96.5 g
25	Water	175.0 g
	HCl (37%)	0.3 g
	EDTA (5% aqueous solution)	5.2 g
	KBrO ₃ (1.5%)	6.0 g
	CuSO ₄ (1%)	3.0 g
30	sodium formate	0.1 g
	the external phase was Isopar L	100.0 g
	and the amount of primary emulsifier	10.0 g

The primary emulsifier used was a mixture of surfactant SE1 or SE2 and a low HLB surfactant (Span 80). The polymerisation initiator used was KBrO₃/Na₂S₂O₅ and the reaction procedure described above for water soluble, redox initiators was used. Comparative runs were carried out

using conventional polymeric surfactants with the low HLB surfactant. The coagulum levels are included in Table 2 below.

Table 2

Ex No	Primary emulsifier				coagulum (%)
	polymeric		low HLB		
	type	amt (wt%)	type	amt (wt%)	
3a.1	SE2	20.00	Span 80	80.00	0.70
3a.1C	Pol2	20.00	Span 80	80.00	0.70
3a.2	SE1	25.00	Span 80	75.00	0.60
3a.2C	Pol3	25.00	Span 80	75.00	0.60
3b.1	SE2	20.00	Span 80	80.00	0.50
3b.1C	Pol2	20.00	Span 80	80.00	0.50
3b.2	SE1	25.00	Span 80	75.00	0.80
3b.2C	Pol3	25.00	Span 80	75.00	0.60

Example 3

A number of personal care emulsions were made up using the product of SE2 as emulsifier.

5 Further materials used in these formulations are:

Arlamol S7 propoxylated fatty alcohol and cyclomethicone ex Uniqema

Arlamol HD isoparaffin emollient oil ex Uniqema

Florasun 90 sunflower oil ex Floratech

Atlas G-2330 sorbitol 30EO derivative ex Uniqema

10 Germaben II preservative ex Sutton

Oxyne K antioxidant ex Merck

Example AE3a

A light moisturising cream was made up as follows:

	Material	amount (pbw)
A	SE2	1
	Arlamol S7	3
	Arlamol HD	6
B	Atlas G-2330	4.5
	MgSO ₄ ·7H ₂ O	0.8
	water	83.7 (to 100)
C	Germaben II	1

Components A and B were made by mixing the individual starting materials and were heated to

15 about 75°C, the Germaben was added to component B. Component B was then added slowly to

Component A under intensive stirring (600 rpm; 10 Hz). After completion of the addition the emulsion was homogenised for 1 minute at 13800 rpm (230 Hz). The emulsion had a Brookfield viscosity [spindle E at 1.5 rpm (0.025 Hz)] of 273000 MPa.s and remained stable under storage at 5°C for at least 1 month.

5 Example AE3b

A liquid body milk formulation was made up as follows:

	Material	amount (pbw)
A	SE2	2
	Arlamol S7	6
	Arlamol HD	12
B	Atlas G-2330	4
	MgSO ₄ .7H ₂ O	0.7
	water	74.2 (to 100)
C	Germaben II	1

The same formulation method was used as described in AE3a. The product emulsion had a Brookfield viscosity [spindle B at 6 rpm (0.1 Hz)] of 4800 MPa.s.

Example AE3b

- 10 A liquid body milk formulation was made up using vegetable oils as the disperse phase as follows:

	Material	amount (pbw)
A	SE2	2
	Florasun 90	12
	Oxynex K	0.05
B	glycerine	3.5
	MgSO ₄ .7H ₂ O	0.5
	water	65.45 (to 100)
	Germaben II	1

Components A and B were made by mixing the individual starting materials and were heated to about 75°C. Component B was then added slowly to Component A under intensive stirring (600 rpm; 10 Hz). After completion of the addition the emulsion was homogenised for 1 minute at 13800 rpm (230 Hz). The emulsion had a Brookfield viscosity [spindle B at 6 rpm (0.1 Hz)] of 11660 MPa.s.

Claims:

- 1 an amide surfactant compound of the formula (I):



where:

- 5 R^1 is a polymeric hydrophobe group, in which the units that make up the polymer contain at least 4 carbon atoms, there are at least 5 units in the polymeric group and the polymeric group contains at least 30 carbon atoms in total;
- R^2 is a group $CH_2-(CHOR^4)_n-CH_2OR^4$ where n is from 3 to 6 and R^4 is hydrogen, C_1 to C_6 alkyl or a saccharide residue, containing at least 2 free hydroxyl groups;
- 10 R^3 is hydrogen, C_1 to C_{22} hydrocarbyl, a substituted alkyl group; or
- R^3 is independently as defined above for R^2 .

- 2 An amide surfactant as claimed in claim 1 of the formula (Ia):



where

- 15 R^{1a} is a polymeric hydrophobe including a polyisobutylene group particularly containing an average of from 40 to 200 carbon atoms; and
- R^2 and R^3 are as defined in claim 1.

- 3 An amide surfactant as claimed in claim 2 in which the group R^{1a} is of the formula (IIa):



20 where

- one of R^{5a} and R^{5b} is a hydrogen atom and the other is a polyisobutylene group; and
- R^6 is a group - OX where X is hydrogen atom, a metal, an amine or a hydrocarbyl group; a hydroxyalkyl group; an alkoxyalkyl group; or
- R^6 is a hydrophilic group.

- 25 4 An amide surfactant as claimed in claim 3 in which one of R^{5a} and R^{5b} is a hydrogen atom and the other is a polyisobutylene group containing an average of from 40 to 200 carbon atoms.

- 5 An amide surfactant as claimed in claim 3 in which X is a C_1 to C_{20} hydrocarbyl group; a C_2 to C_6 hydroxyalkyl group; or a (C_1 to C_4)alkoxy(C_2 to C_6)alkyl group.

- 30 6 An amide surfactant as claimed in claim 3 in which R^6 is a hydrophilic group which is an amido group of the formula $-NR^2R^3$ where R^2R^3 are each independently as defined in claim 1.

- 7 An amide surfactant as claimed in claim 1 of the formula (Ib):

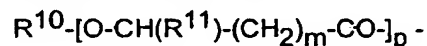


where

R^{1b} with the adjacent carbonyl group is a residue of polyhydroxycarboxylic acid polyester group, containing an average of from 50 to 200 carbon atoms; and

R^2 and R^3 are as defined in claim 1.

- 5 8 An amide surfactant as claimed in claim 7 in which the group R^{1b} is of the formula:



where

R^{10} is hydrogen or the residue of a C_2 to C_{22} fatty acid;

R^{11} is hydrogen or a C_1 to C_{15} alkyl group;

10 m is from 4 to 20; and

p is on average from 4 to 20.

- 9 An amide surfactant as claimed in either claim 7 or claim 8 in which the group R^{1b} with the adjacent carbonyl group is a residue of poly(12-hydroxystearic acid) or poly(caprolactone).
- 10 A water in oil emulsion including at least one compound as claimed in any one of claims 1 to 15 9 as an emulsifier and/or stabiliser
- 11 A dispersion of a solid in an aqueous or non-aqueous liquid including at least one compound as claimed in any one of claims 1 to 9 as a dispersant.
- 12 A method of making polyacrylamide by inverse emulsion polymerisation which comprises dispersing an aqueous solution of polymerisable monomers including acrylamide in an oil 20 phase the system also including a water in oil surfactant including at least one compound as claimed in any one of claims 1 to 9 and polymerising the polymerisable monomers to form a colloidal suspension of particles, of a solution or dispersion of the resulting polyacrylamide polymer in water, in the oil.
- 13 A method of water treatment that includes diluting an inverse polyacrylamide emulsion, 25 made by the method claimed in claim 12 into the water to be treated such that the emulsion is inverted releasing the polyacrylamide into the water and emulsifying the oil phase in the dilution water.
- 14 An emulsion explosive in which an aqueous phase including an oxidiser is emulsified in a fuel phase and in which at least one compound as claimed in any one of claims 1 to 9 is 30 included as an emulsifier for the aqueous phase.
- 15 A method of causing explosions which method includes introducing an emulsion explosive as claimed in claim 14 into a rock formation and subsequently detonating the explosive.

- 16 A personal care composition which is or includes an aqueous phase dispersed or emulsified in an oil phase which includes as a dispersant and/or emulsifying agent at least one compound as claimed in any one of claims 1 to 9.
- 17 A method of making an oil in water cosmetic or personal care emulsion containing water in oil droplets which includes forming a mixture of an oil phase and oil in water primary emulsifier for dispersing oil in an aqueous phase including at least one compound as claimed in any one of claims 1 to 9 and adding to the oil mixture under stirring to an aqueous phase.
- 18 An agrochemical emulsion or dispersion, in which at least one compound as claimed in any one of claims 1 to 9 is included as an emulsifier or dispersant.
- 19 An agrochemical emulsion or dispersion as claimed in claim 18 which is:
- i an agrochemical emulsion including an agrochemically active material which is dissolved, dispersed or emulsified in a first liquid component, the first liquid component being emulsified in a second liquid component; or
 - ii an agrochemical formulation including an agrochemically active material which is dissolved, dispersed or emulsified in a first liquid component, a second liquid component being emulsified in the first liquid component; or
 - iii an agrochemical dispersion in which a solid component is dispersed in a liquid phase.
- 20 An agrochemical emulsion or dispersion as claimed in either claim 18 or claim 19 in which the agrochemically active material(s) is one or more plant growth regulators, herbicides, and/or pesticides.
- 21 An agrochemical emulsion or dispersion as claimed in claim 20 in which the agrochemically active material is one or more of: water soluble, non-selective, herbicides selected from triazines, substituted ureas, sulphonyl ureas, pyridine carboxylic acids, aryloxy alkanolic acids, 2-(4-aryloxy- phenoxy)propionic acids and bis-carbamates; fungicides selected from thiocarbamates, strobilurins, dicarboximides, benzimidazoles, azoles and inorganic fungicides; benzoyl urea insecticides; and tetrazine acaricides.
- 22 An invert drilling fluid which is an emulsion of an aqueous brine phase in an oil, which fluid further includes a dispersion of a weighting agent, including as an emulsifier and/or dispersant at least one compound as claimed in any one of claims 1 to 9.
- 23 A rolling oil emulsion which is an oil in water emulsion of a rolling oil, and which includes as an emulsifier at least one compound as claimed in any one of claims 1 to 9.

- 24 A rolling oil concentrate which is a solution in a rolling oil of at least one at least one compound as claimed in any one of claims 1 to 9, which solution is emulsifiable in water to form a rolling oil emulsion.
- 5 25 A cutting fluid emulsion which is an emulsion, including an oil phase and an aqueous phase, which includes as an emulsifier and/or a stabiliser at least one compound as claimed in any one of claims 1 to 9.
- 10 26 A cutting fluid concentrate which is a solution in an oil phase of at least one compound as claimed in any one of claims 1 to 9, which solution is emulsifiable in water to form a cutting oil emulsion.

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(54) Title: **POLYMERIC SURFACTANTS**

(57) Abstract: Amide surfactant compound of the formula (I): $R^1-CO-NR^2R^3$, where R^1 is a polymeric hydrophobe group; R^2 is a group $CH_2-(CHOR^4)_n-CH_2OR^4$ where n is from 3 to 6 and R^4 is hydrogen, C_1 to C_6 alkyl or a saccharide residue, containing at least 2 free hydroxyl groups; and R^3 is hydrogen, C_1 to C_{22} hydrocarbyl, substituted alkyl, or R^3 is independently as defined above for R^2 , are useful as emulsifiers and/or stabilisers for water in oil emulsions, or as dispersants for solids in aqueous or non-aqueous liquids. Particular end use applications include as emulsifiers, stabilisers or dispersants in making polyacrylamide, particularly for water treatment, by inverse emulsion polymerisation; emulsion explosives; personal care compositions including an aqueous phase dispersed or emulsified in an oil phase; agrochemical emulsions and concentrates, and cutting fluid emulsions and concentrates.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 00508 A (ICI) 6 January 1994 (1994-01-06) claims 1-12	
A	EP 0 947 243 A (BASF) 6 October 1999 (1999-10-06) claims 1-10	

☐ Further documents are listed in the continuation of box C.

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